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Quantitative Spectrum Analysis

By

Arata Iwamura

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Part I. On the electrodes used in quantitative emission-spectrum analysis

There are several methods of carrying out quantitative emission-spectrum analysis, such as A. de Gramont's "test method", Gerlach and Schweitzer's "absolute method", or the "internal standard method" and so forth. Of these, the one first mentioned is widely used.

In these methods of analysis, it is necessary to prepare a large number of electrodes composed of standard samples the main constituent (or constituents) of which contains varying amounts of the element in question, and also electrodes of the sample to be analysed, which are taken to be nearly the same as those of the standard samples.

We shall now consider various forms of electrodes when the sample to be analysed is given in the form of (1) a solution, or (2) a soluble or insoluble non-conducting solid or powder.

1. The sample to be analysed is given in the form of a solution

Such a sample may be employed either

a. in the form of the solution itself, or

b. in the form of a solid electrode prepared from zinc oxide, calcium oxide or magnesium oxide mixed with the solution.

1. a. In this case Delachanel and Mermot's electrodes[1] are convenient, but they have the defect that a glass capillary is easily broken,

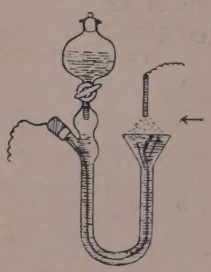
1. Baly-Spectroscopy II Fig. 43. a. p. 120.

and the solution soon evaporates and is easily dispersed. E. Becquerel's electrodes[1] are simple and convenient when excited with small sparks, but a defect similar to the above results when the sparks are large. In this case it is better to use the electrodes employed by Hartley,[2] but it is somewhat difficult to keep the electrodes wet with the solution uniformly, so as not to interrupt the spark during the time of exposure.

The gold electrodes of Pollok and Leonard are also used for a sample in the form of solution, but if the solution is very dilute, a large volume of solution and long time of sparking are required in order to obtain a good spectrogram. As the evaporation and dispersion of the solution are greater at the beginning than at the end of sparking, the intensities of the required spectrum lines are not kept constant.

Such are the most detrimental phenomena in the practical procedure of the quantitative emission-spectrum analysis of a solution. The present writer found that by using the apparatus shown in Fig. 1. constancy in the spectra of the solution is attained. The figure is one half the actual size and is self-explanatory.

Fig. 1



During the sparking, the surface of the solution should be kept at a definite height by regulating the speed at which the solution is dropped.

If the lower electrode is wet with the solution, a definite noise of sparks is constantly heard, but if the lower electrode gets dry, the noise changes and sounds destructive.

The radius of the funnel containing the lower gold electrode is made a little larger than the distance between the electrodes, otherwise sparks pass between the edge of the funnel and the upper electrode. The glass or quartz capillary through which the solution ascends is often broken by condensed sparks, so that two or three thin gold plates, $2 \times 10 \times 0.3\text{mm}^3$, are substituted for it. The upper gold electrode consists of gold wire of 2 mm. dia. The paths of the discharges are shown by the dotted lines in Fig. 1 and the spark is viewed and spectrographed in the direction of the arrow.

1. Baly-Spectroscopy II Fig. 43. b. p. 120.
2. „ „ Fig. 44. „

Another metal may be substituted for the gold, if necessary.

1. b. To convert a liquid sample into a conducting solid. It is often convenient to convert a given sample of solution into a conducting solid. According to Baly (Vol. II, p. 119) "the dry cones (purified carbon cones) are boiled in an aqueous solution of the required metallic salt. If available, the nitrate is the most suitable salt to use, since metallic oxide is formed simply by heating the cones at a red heat. In this case, the treatment with the solution and the subsequent heating may be repeated several times." This method is suitable for the purpose of qualitative spectrum analysis, but not for quantitative spectrum analysis, because the homogeneous adsorption of a definite amount of a salt of known concentration by carbon can not be expected. The adsorption of some metallic salt on wood charcoal is irreversible. Some metallic ion loses its charge and is deposited on the pores of the charcoal and is not removed by simply washing it with water, the remaining solution becoming strongly acidic. This is a marked phenomena when charcoal is used as adsorbent. The same phenomenon will take place in a less degree when a less porous carbon such as gas carbon or artificial graphite is used, and homogeneity of the sample electrode thus prepared is highly improbable. Even though it is assumed to be really homogeneous, the amount of salt adsorbed is not proportional to the concentration of the solution.

According to colloidal chemistry, the relation

$$\frac{x}{m} = aC^{\frac{1}{n}} \quad \text{holds at constant temperature,}$$

where

x=the amount of salt adsorbed on adsorbent (carbon)
m=mass of adsorbent (carbon)
C=concentration of the salt solution and n=constant.

If m is taken to be constant, say $m=1$. gm. or 10 gms. in each case, then

$$x = A.C^{\frac{1}{n}}, \qquad \text{where } A = am.$$

Thus we see x is proportional to $C^{\frac{1}{n}}$, and not to C, showing that the amount of salt adsorbed by carbon from a solution of kown concentration at constant temperature is not proportional to the concentration of the salt solution. If n is known, it may be adequate to use such electrodes in quantitative emission spectrum analysis, provided the other conditions are quite satisfactory.

An electrode of a uniform sample may be obtained according to the methods described below:

(a) 10 gms. of pure carbon or powdered carbon made from molasses are put into a mortar, and a definite quantity of sample solution, (for standard electrodes, definite quantities of known concentrations of an element) is added to it and well mixed. Then 9.5 gms. of cane sugar molasses are added to give proper consistency, and the mixed mass thus produced is formed into a circular disc or rectangular stick by means of an aluminium mould and heated gently over a Bunsen burner,—heating in an electric furnace under diminished pressure will produce better results more quickly. All this process takes about an hour. Spectrograms taken with such electrodes are shown in PL. I. a, b & c.

(b) To the solution mixed with concentrated hydrochloric acid in such a proportion that the concentration of the acid becomes 6 *N*, pure zinc oxide, pure magnesium oxide, or pure calcium oxide is added and after thorough mixing the mixture is moulded into electrodes and dried.

2. Soluble or insoluble non-conducting solid or powder

In the case of determining very small quantities of lead contained in zinc oxide, the usual method is to dissolve the oxide in hydrochloric or sulphuric acid, and to examine the solution by means of spark spectra, using pure gold or pure zinc electrodes.

But in that method the concentration of lead in the zinc solution is naturally smaller than that in zinc oxide in the solid state, which makes the quantitative estimation of the lead in the original zinc oxide very difficult.

In Sawyer and Becker's[1] method zinc oxide is made to adhere to asbestos threads which are moistened with a zinc chloride or sulphate solution to render them conductive. But the zinc oxide is soon dispersed as the high-tension alternating current passes through the thread and consequently this method can not be used to prepare good long-lasting electrodes.

According to Baly[2] A. de Gramont's method of converting a non-conductor into a conductor is stated as follows:

"If the mineral is a non-conductor, it may be fused with Na_2CO_3

1. Baly-Spectroscopy II, p. 88.
2. „ II, p. 149.

in a small platinum-capsule, and the spark spectra of the melted material examined. By the use of known weight of mineral and alkali, an estimate of the relative proportion of the metallic constituents present in the mineral can be made." This method is generally recommended for the quantitative emission-spectrum analysis of a non-conducting insoluble solid mass or powder. But from the practical point of view, the above method is found still inconvenient in the following points: (1) The sample becomes diluted, (2) The fused mass is hygroscopic, (3) The spectrum is complicated by the presence of platinum lines, and (4) The process of fusing the sample with an alkali requires rather a long time.

After several trials the present writer succeeded in procuring suitable electrodes which have no such defects as those mentioned above. The manner of preparation is as follows:

The sample of zinc oxide and some pure carbon (activated carbon) are kneaded in a mortar together with some cane-sugar molasses, moulded in an aluminium tube, and heated on a Bunsen-burner. After cooling, the aluminium is removed, and the resulting mass is used as electrodes. This process has, however, the demerit that it causes some of the lead to be lost, as it is reduced in the presence of reducing substances at the temperature of a Bunsen-burner.

The method of cementing zinc oxide with a zinc chloride solution may also be used. In using this method it must be borne in mind that a trace of lead is frequently detected even in carefully purified zinc chloride. Instead of using a zinc chloride solution, if some zinc oxide is added little by little to 3N-HCl solution contained in a mortar and is stirred, it gradually dissolves, leaving some zinc oxide in suspension. By further addition of zinc oxide, it is transformed into a pasty mass which solidifies rapidly and conducts electricity.

This paste, when properly moulded and set, is suitable for use as the sparking electrodes. For the purpose of increasing the conductivity, some electrolyte such as KNO_3, K_2SO_4 etc. or a metal powder such as aluminium may be added at the time of kneading. The solidity of the mass depends on the proportions of the components and the method of mixing them, as is seen in the case of forming a magnesia cement from magnesium oxide and magnesium chloride.

The following was found to give a good result: 30 grammes of zinc oxide is gradually added to 35 c.c. of 6N-HCl in a porcelain mortar, kneaded and moulded before it sets; it is then dried in an

air-oven and used. Zinc oxide containing some carbonate behaves similarly. This procedure is applicable for the preparation of conducting solid electrodes from carbonates and basic carbonates of other metals, mixing them with pure zinc oxide, magnesium oxide or calcium oxide for cementing purpose.

Oxides and carbonates of metals are generally bad conductors of electricity, but they are soluble in mineral acids, giving homogeneous solutions. Quantitative spectrum analysis is usually performed with such a solution. But it is more convenient to transform them into solid masses conducting electricity in the way described above and to use them directly as sparking electrodes for the determination of minute quantities of elements contained in such substances.

Insoluble, non-conducting powders may also be transformed into conducting solid electrodes by similar treatment. Spectrograms taken with such electrodes by means of a small Hilger quartz spectrograph are shown in PL. II; *a* showing the one obtained with electrodes containing powdered natural silver ore and prepared in the above mentioned way. Silver lines at $\lambda = 2934$, 2902, 2897, 2661, 2535, 2507 and 2481–71 Å are seen in *a*.

Silica sand, talc, siliceous ores of gold and silver and such like are insoluble in chemicals and also non-conductors of electricity. All such substances in a finely powdered state can be transformed into a conducting solid electrode when mixed with zinc oxide and zinc chloride or zinc oxide and hydrochloric acid, or magnesium oxide and HCl, or calcium oxide and HCl.

Photo *b* in PL II. shows a spectrogram of talc + ZnO + HCl
„ *c* „ „ that of ZnO + HCl.

Summary:

(1) A modification of the gold electrodes of Pollok and Leonard so as to keep their sparking conditions constant for a longer period of time with very dilute solutions is described.

(2) A method of converting a liquid sample into a conducting solid electrode is described.

(3) A method of converting samples of soluble or insoluble non-conducting materials into conductive solid electrodes to be used in quantitative emission-spectrum analysis is given.

Plate I

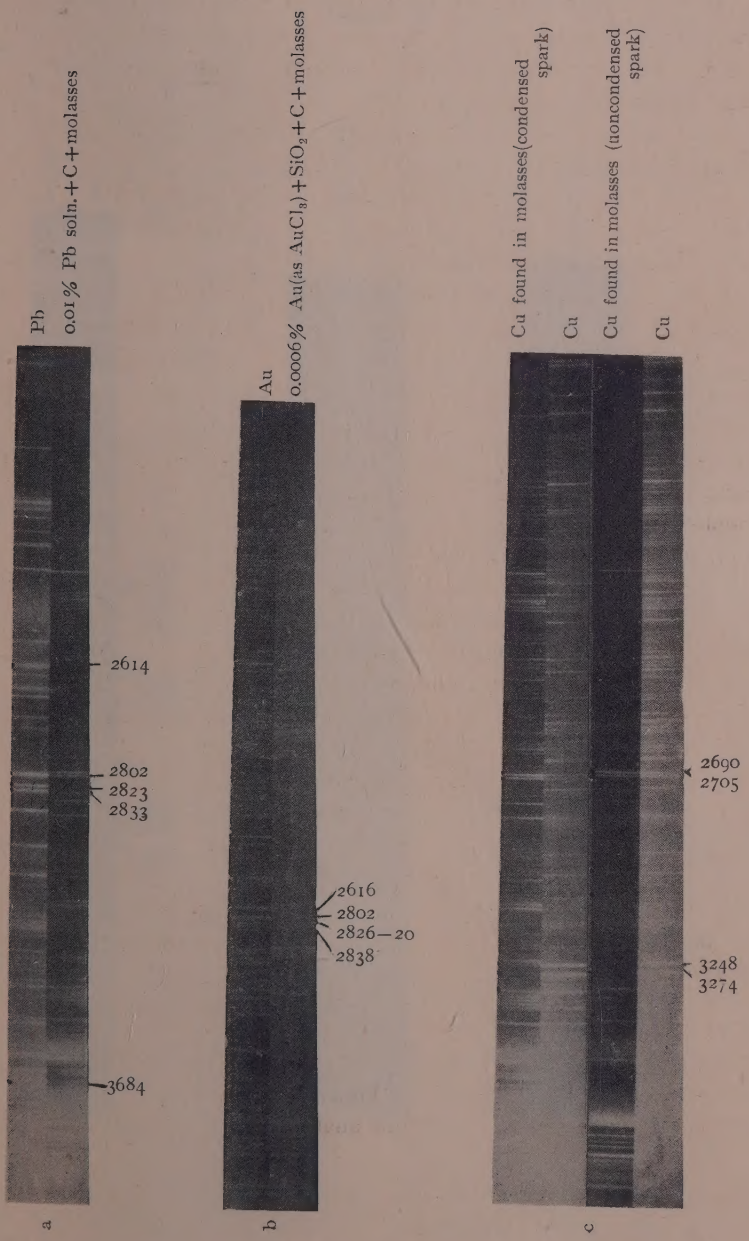
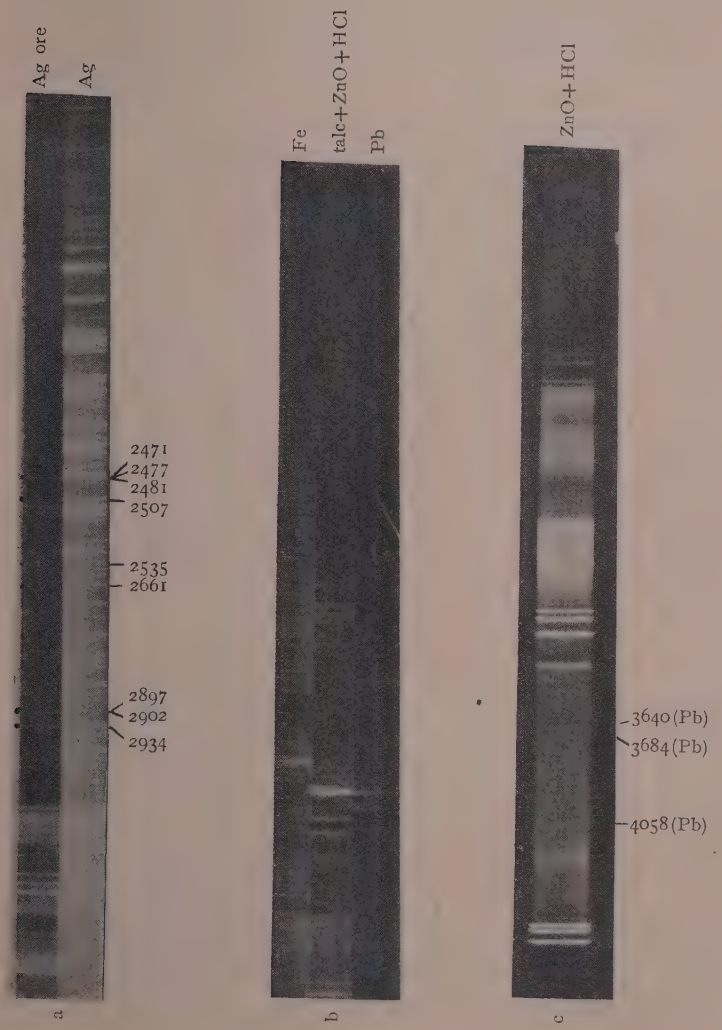

Pb
0.01% Pb soln.+C+molasses
2614
2802
2823
2833
3684
a
Au
0.0006% Au(as $AuCl_3$)+SiO_2+C+molasses
2616
2802
2826—20
2838
b
Cu found in molasses(condensed spark)
Cu
Cu found in molasses (uncondensed spark)
Cu
2690
2705
3248
3274
c

Plate II


Ag ore
Ag
2471
2477
2481
2507
2535
2661
2897
2902
2934
a
Fe
talc+ZnO+HCl
Pb
b
ZnO+HCl
3640(Pb)
3684(Pb)
4058(Pb)
c

Part II. Quantitative emission-spectrum analysis of lead contained in zinc oxide

1. Sample Electrodes.

For the purpose of spectrographically determining very small quantities of lead contained in zinc oxide, the oxide was first transformed into a solid conducting mass by treating merely with hydrochloric acid and then dried. A most suitable electrode was prepared in the following way :

20 grams of zinc oxide were gradually added to 23.3 c.c. of 6 N-HCl in a porcelain mortar and this was constantly agitated, kneaded, and then moulded in a wooden mould before it was quite set, and the product was dried in an air-oven. The solid mass thus prepared was a round tablet, 3 cms. in diameter and 3 mm. thick, a round hole being made at its centre. Two such tablets containing zinc oxide having no foreign impurities were employed as the electrodes; the hydrochloric acid also contained no foreign impurities, as a very pure hydrochloric acid is easily obtained.

2. The apparatus used and the method of experiment.

To excite sparks between a pair of such electrodes, a transformer giving 10 K.V. in the secondary was used. Self inductance of a magnitude of about 62,000 cms. was always inserted in the secondary circuit. The light from an uncondensed spark between the electrodes was focused by means of a quartz lens on the slit of a small Hilger quartz spectrograph and spectrograms were thus obtained. When the sample contains a trace of lead, the lead lines at $\lambda = 4058$, and 3684 Å are always detected on the plate.

The photographic density of a line was recorded by means of a Moll's recording microphotometer and for practical purposes the maximum heights of the curve for these lines measured from the neighbouring background were taken as a measure of the practical intensities of these lines.

3. Reproducibility of the spectrograms of zinc oxide electrodes containing lead.

In spectrographical quantitative analysis of metals and alloys, it is generally assumed that the result is always reproducible, within a range of permissible errror under certain definite conditions of experiment.

With the present electrodes it is necessary to show experimentally that the electrodes always give a reproducible result.

This was proved to be the case as is shown in the following spectrograms and the corresponding microphotometry curves given in plates I and II.

From curves I. a.

	$d(\lambda=4058)$	Δ	$\Delta\%$	$d(\lambda=3684)$	Δ	$\Delta\%$	$d(\lambda=3640)$	Δ	$\Delta\%$
	(13.4)	——	——	15.5	$-\frac{7}{1557}$	$-0.5-$	6.8	$-\frac{5}{685}$	$-0.8-$
	18.1	$-\frac{5}{1815}$	$-0.3-$	15.6	$-\frac{3}{1557}$	$+0.2-$	6.9	$+\frac{5}{685}$	$+0.8$
mean:	$\frac{18.2}{18.15}$	$+\frac{5}{1815}$	$+0.3-$	$\frac{15.6}{15.57}$	$+\frac{3}{1557}$	$+0.2-$	$\frac{(9.6)}{6.85}$	——	——

From curves I. b.

	$d(\lambda=4058)$	Δ	$\Delta\%$	$d(\lambda=3684)$	Δ	$\Delta\%$	$d(\lambda=3640)$	Δ	$\Delta\%$
	34.4	$+\frac{210}{3230}$	$+6.5+$	30.3	$+\frac{167}{2863}$	$+5.8+$	16.6	$+\frac{93}{1567}$	$+5.9+$
	30.0	$-\frac{230}{3230}$	$-6.1+$	27.5	$-\frac{113}{2863}$	$-3.9+$	15.4	$-\frac{27}{1567}$	$-1.7+$
	$\frac{32.5}{32.30}$	$+\frac{20}{3230}$	$+0.6+$	$\frac{28.1}{28.63}$	$-\frac{53}{2863}$	$-1.9-$	$\frac{15.0}{15.67}$	$-\frac{67}{1567}$	$-4.3-$
M:									

From curves II. A.

	$d(\lambda=4058)$	Δ	$\Delta\%$	$d(\lambda=3684)$	Δ	$\Delta\%$	$d(\lambda=3640)$	Δ	$\Delta\%$
	74.4	$+\frac{137}{7303}$	$+1.9-$	66.7	$-\frac{37}{6707}$	$-0.6-$	48.9	$-\frac{3}{4893}$	$-0.1-$
	73.2	$+\frac{17}{7303}$	$+0.2+$	68.5	$+\frac{143}{6707}$	$+2.1+$	51.3	$+\frac{243}{4893}$	$+5.0-$
	71.5	$\frac{153}{7303}$	$-2.1-$	66.0	$-\frac{107}{6707}$	$-1.6-$	46.6	$-\frac{233}{4893}$	$-4.8-$
M:	73.03			67.07			48.93		

Δ=deviation from the arithmetical mean.
d=photographic density in mm.

From the above figures we see that the result is always reproduced within 6.5% to -6.1%.

The sensibility of the recording microphotometer was tested by placing a plate in the plate holder of the apparatus, and the photometric records were taken twice as shown in plate II. B.

The height of the curve corresponding to a line was measured to a fraction of a mm. and this is given in the following tables.

From PL. III.

	Intensity Measure								
λ_{Pb} / No.	d 4058			d 3684			d 3640		
	mm	Δ	Δ%	mm	Δ	Δ%	mm	Δ	Δ%
1	30.2	$-\frac{30}{3050}$	−0.98+	26.7	$-\frac{15}{2685}$	−0.56+	15.8	$-\frac{15}{1595}$	−0.94+
2	30.8	$+\frac{30}{3050}$	+0.98+	27.0	$+\frac{15}{2685}$	+0.56+	16.1	$+\frac{15}{1595}$	+0.94+
mean	30.50			26.85			15.95		

From PL. II c & d.

	Intensity Measure								
λ_{Pb} / No.	d 4058			d 3684			d 3640		
	mm	Δ	Δ%	mm	Δ	Δ%	mm	Δ	Δ%
1	71.5	$+\frac{5}{7145}$	+0.06+	66.0	$+\frac{5}{6595}$	+0.08−	46.6	$+\frac{15}{4645}$	+0.35−
2	71.4	$-\frac{5}{7145}$	−0.06+	65.9	$-\frac{5}{6595}$	−0.08−	46.3	$+\frac{15}{4645}$	−0.35−
mean	71.45			65.95			46.45		

The recording photometer is sensitive within a range of ±1.% of error.

4. Sensibility of the spectrographic analysis of *Pb* contained in ZnO.

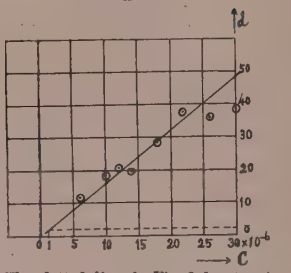
The sensibility is usually expressed by the smallest detectable amount of an element contained in a main constituent. In the present case, this corresponds to the smallest detectable height of the *Pb* line $\lambda = 4058$ Å on the microphotometer curve and this is extrapolated in the following way. A series of spectrograms were taken of sparks emitted from electrodes containing a varying amount of lead, and the practical intensities of the line were measured on microphotometer curves for various contents of lead, and a curve connecting intensity of the line and the corresponding amount of lead was drawn as shown in the accompanying figure and table (see also PL. II. C).

The extrapolation of this curve gives the minimum detectable limit in the present method, i. e. the sensitivity of the method.

C % *Pb*	$d(\lambda=4058$ Å)
0.0030	38.6
0.0026	36.0
0.0022	37.8
0.0018	28.4
0.0014	19.6
0.0012	20.5
0.0010	18.5
0 0006	11.9

See PL. II. C.

Fig. 2



The dotted line in Fig. 2 denotes the density of the back ground of the plate

The sensibility is therefore found to be 1×10^{-6} under the conditions of the present experiment. This value may vary within certain limits depending upon the conditions of the photographic plates and the method of developing.

5. Examples.

For practical purposes, the present experiment was confined to the determination of the quantity of lead contained in zinc oxide, ranging from 6×10^{-6} to 3×10^{-5} and the method gave the following result.

One of the spectrograms and photometer records are shown in PL. III—1.2.3.

Examples. (S denotes the % of Pb in the sample taken)

(I)		(II)		(III)	
% *Pb*	*d*	% *Pb*		% *Pb*	*d*
0.0090		0.0070		0.0070	
S	—	S	—	S	—
0.0050	—	0.0030	—	0.0050	—
S	—	S	—	S	—
0.0025	—	0.0020	18.4 → 5.0	0.0040	—
S	—	S	13.4 → 5.9	S	—
0.0012	9.0 → 3.6	0.0006[3]	7.5	0.0030	27.5 → 0.3
S	5.4 → 2.2			S	27.2 → 2.5
0.0004	3.2			0.0020	25.0
by proportionality		by proportionality		by proportionality	
$8\times\frac{2.2}{5.8}=3$		$13.7\times\frac{5}{10.9}=6.3$		$10\times\frac{0.3}{2.8}=1.1$	
$S=0.0004+0.0003=0.0007$		$S=0.0020-0\ 00063=0.00137$		$S=0.0030-0.00011=0.00289$	

6. Chemical Analysis.

It will be not without interest to compare the above method with the ordinary method of chemical analysis to determine a minute trace of lead. This was done in the following way:

100 grams of the zinc oxide sample to be analysed were dissolved in concentrated hydrochloric acid and the solution was saturated with hydrogen sulphide gas.

After standing overnight, the precipitate that settled was filtered, washed with water containing hydrogen sulphide, dissolved in hot dilute nitric acid, and the nitric acid solution was evaporated in a water bath nearly to dryness. Some hot water was then added to the residue and the basic bismuth nitrate thus separated was separated by filtration and washed (when estimation of bismuth is not required, evaporation to only a small bulk of solution is sufficient).

The filtrate and the wash water were united, acidified with concentrated nitric acid and electrolysed according to the usual method. The deposit on platinum anode was washed, dried, heated at 180°C for 1 hr. and the lead peroxide thus obtained was iodometrically determined. The results are shown in the following table:

No. of Sample.	I	II	III
Pb found (%)	0.0006	0.00133	0.0027

7. Comparison of the results of spectrographical analysis with those of chemical.

Let S denote the value of lead spectrographically obtained and C that chemically found.

Sample.	I	II	III
S	0.0007	0.00137	0.00289
C	0.0006	0.00133	0.0027
Δ	0 0001	0.00004	0.00019
Δ%	$(\frac{100\times 1}{7})14.^{+})$	$(\frac{100\times 4}{133}=)3.^{-}$	$(\frac{100\times 19}{289}=)7.^{-}$

As is shown in the above table the spectrographical results are generally somewhat higher than the chemical ones, but they are of the same order of magnitude.

It will be noticed that the spectrographic method of analysis has advantage over the chemical in the following points: (1) its rapidity, (2) its simplicity, (3) no loss of a sample during analysis, (4) quantity of a sample required for analysis is comparatively very small, (5) the

result of the experiment is recorded almost free from any personal errors and (5) the method is especially suitable for microanalysis.

It must, however, be remembered that this method often introduces comparatively large errors which may perhaps be due to unavoidable fluctuation of sparks.

8. Summary.

1. Electrodes consisting of a zinc oxide sample containing lead, were prepared for the purpose of quantitative emission-spectrum analysis.

2. The reproducibility of the spectrograms of the electrodes was tested, and was shown to be within -4.8 to $+6.5\%$, under the conditions of the experiment.

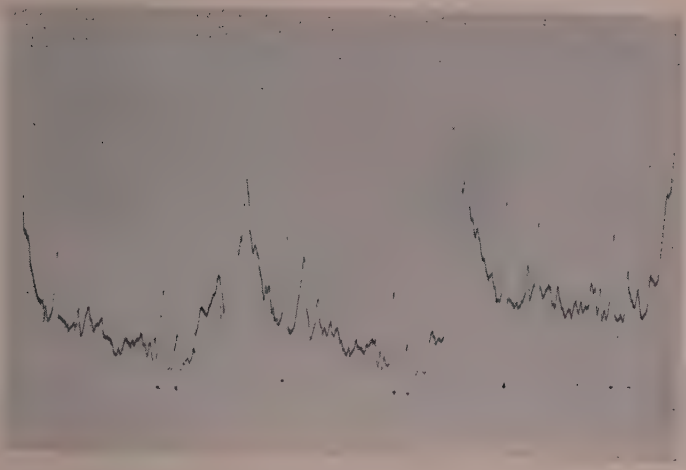
3. The sensibility of this method for estimating lead contained in zinc oxide was determined to be 1×10^{-6} under the conditions used in the experiment.

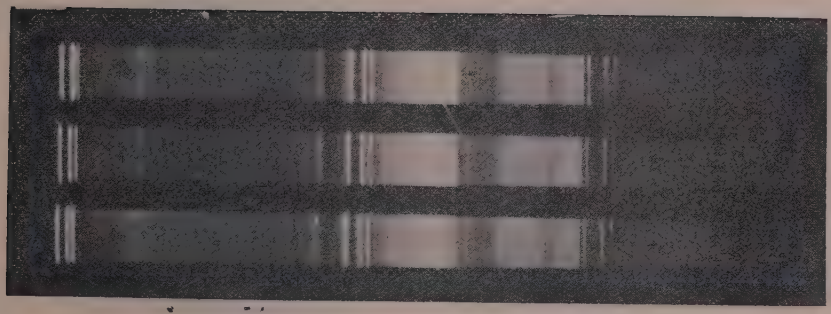
4. The values obtained by emission-spectrum analysis were compared with those found by chemical analysis.

Both were found to be in the same order of magnitude, though the spectrographic values were always somewhat higher than the chemical ones.

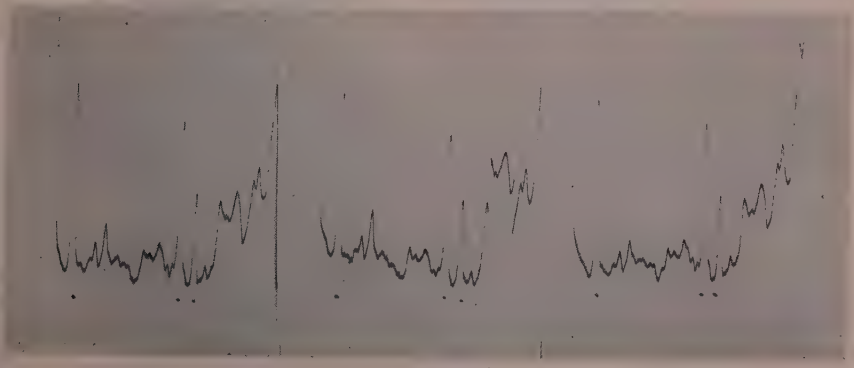
In conclusion, the writer expresses his sincere thanks to Prof. M. Matsui and Prof. M. Kimura, of the Faculty of Science, K. I. U. for their valuable advice and encouragement.

Plate I





b

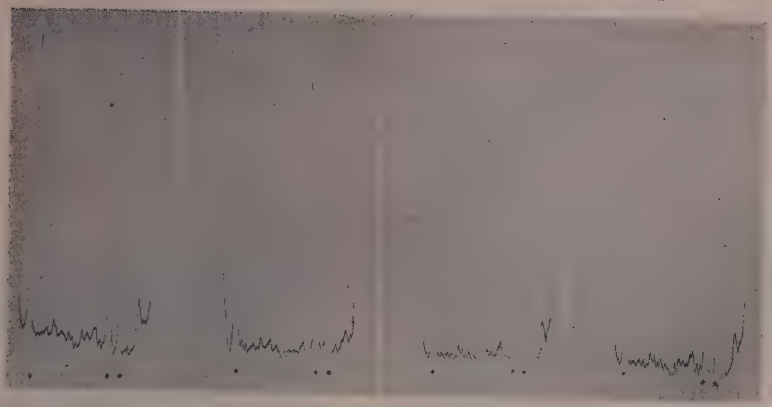


Size : $^4/_5$

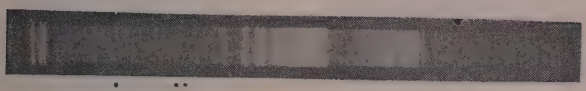
Plate II

a b c d

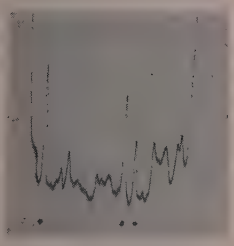
A

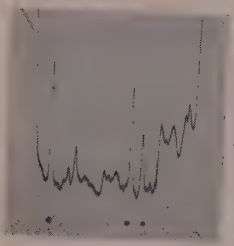


Size : ca $^{2}/_{3}$



B





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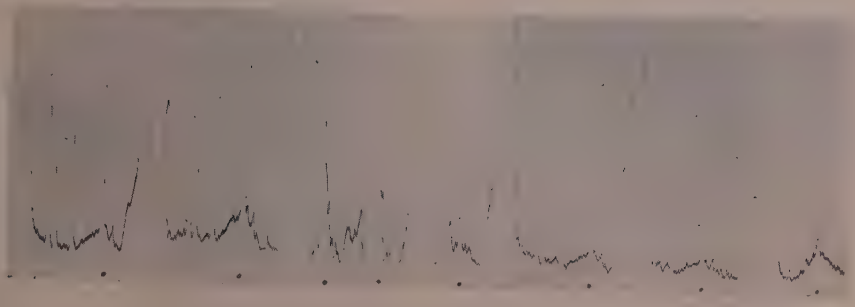
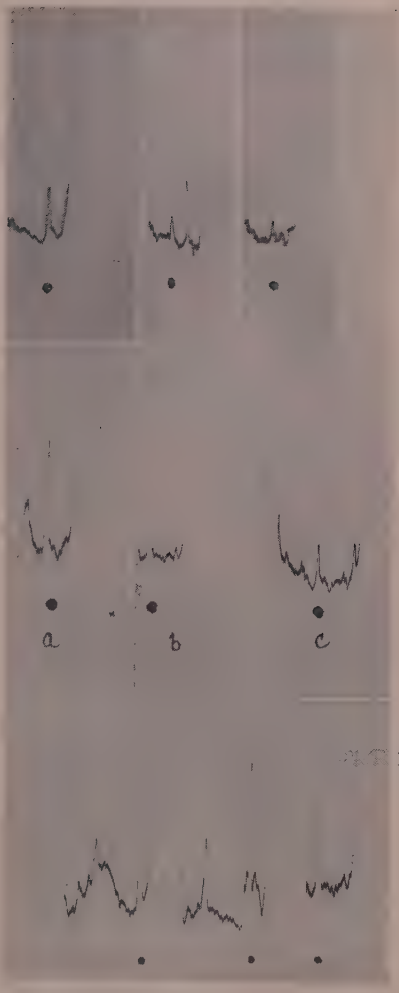
C



Size : ca $^{2}/_{3}$

Plate III

Ex. II.



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Relation between the K Absorption Edge and the $K\beta_2$ Line of *Ni*, *Cu* and *Zn*

By

Suekichi Kawata

(Received November 15, 1930)

Abstract

The relation between the K absorption limit and the $K\beta_2$ line was investigated for the elements *Ni*, *Cu* and *Zn* by the method of comparison to get some light on the process by which X-rays are absorbed. For *Zn* and *Ni* the K limit is on the shorter wave-length side of the $K\beta_2$ line by the amount of 3.0 volts and 2.0 volts respectively, while in the case of *Cu* the K limit and the $K\beta_2$ line are just coincident. The result is compared with that which has been reported just recently by Kievit and Lindsay.[1]

Introduction

Recently evidence has been brought forward by several authors[2] to prove that the X-ray absorption edge does not correspond to the complete removal of an inner electron from the atom, but rather corresponds to the transition to an outer unoccupied orbit. Then, to the question "What is the outer level which gives the main edge?" the answer may be given that for the K absorption edge of the elements here considered it would be the $N_{II, III}$ level.[3] But the transition from the $N_{II, III}$ to the K level gives the line $K\beta_2$. So, if the above consideration is correct the K absorption edge and the $K\beta_2$ line will be just or very nearly coincident. The writer therefore attempted to investigate their relative position by taking photographs of the emission and the absorption spectra on different horizontal

1. B. Kievit and G. A. Lindsay: Phys. Rev., **36**, 648 (1930).
2. See, for example, E. C. Stoner: Phil. Mag., **2**, 97 (1926); K. Chamberlain and G. A. Lindsay: Phys. Rev., **30**, 369 (1927).
3. Cf. D. Coster and J. H. van der Tuuk: Nature, **117**, 586 (1926).

portions of one plate. At the beginning of the experiment he wondered whether the K electron of *Cu* might pass to the N_1 level, because such a transition would form a *Zn*-like atom, and *Cu* might behave peculiarly in contrast to other elements. The experiment was first carried out for the elements from *Fe* to *Zn* with somewhat bad dispersion and a wide slit[1] to see the general trend. The result was that for all the elements, except *Cu*, the absorption limit was distinctly on the shorter wave-length side of the $K\beta_2$ line, but in the case of *Cu* the $K\beta_2$ line and the absorption limit fell so near each other that it could not be decided which was on the shorter side. Hence, he again studied the problem with much higher dispersion and a narrower slit. When the experiment for the elements *Ni*, *Cu* and *Zn* had just been finished a report was published by Kievit and Lindsay[2] showing similar results to those obtained in the present investigation. But in the case of *Ni* they reported that they found the K edge slightly longer in wave-length than the $K\beta_2$ line. This is quite different in the case of the present writer. It seems probable to the writer that the resolution of the line $K\beta_2$ and the satellite $K(\beta''')^3$ was not sufficient in the case of Lindsay and Kievit.

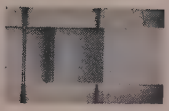
Experimental Method and the Results

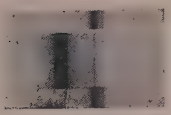
The apparatus and method were the same as in the former research on the satellites of $K\beta_1$ except that the photographic plate was placed further from the slit, and the slit was made narrower to get higher accuracy. As analysing crystal, zinc blende (110) was used in the case of *Ni* and *Cu*, and calcite in the case of *Zn*. As the absorption screen, rolled metal foil was used in every case, the thickness being about 0.01 mm. The dispersion was 9.1 x. u. per mm. for *Ni*, 9.2 x. u. per mm. for *Cu* and 13.8 x. u. per mm. for *Zn*. The width of the slit was such that the width of the $K\beta_2$ line was about 0.06 mm. on the plate throughout. The most difficult thing was to determine which portion was to be considered the real absorption edge. The writer made the measurement by setting the microscope of a comparator on the shortest wave-length limit of the blackening. The point of the intensity maximum of the blackening was also measured as a check in the case of *Zn*, where the $K\beta_1$ line is

1. S. Kawata: These Memoirs, **13**, 383 (1930).
2. loc. cit.
3. S. Kawata: loc. cit.

sufficiently suppressed on the absorption spectrum, and it was found that that point was on the longer wave-length side of the limit by about half the width of the slit. The error in the measurement of the relative position of the K limit and the $K\beta_2$ line can not be much more than $\pm$0.1 x. u. Thus, the result was that for *Cu*, the $K\beta_2$ line and the K limit are just coincident, but for *Ni* and *Zn* the K limit is on the shorter wave-length side of the $K\beta_2$ line, the amount of the separation being about 0.36 x. u. and 0.4 x. u. or 2.0 volts and 3.0 volts respectively. Hence, from the above results, it seems probable that the K electron of *Cu* passes to the $N_{II, III}$ level but those of *Ni* and *Zn* (and also of *Fe* and *Co*) pass to some other outer levels, and it will be remarkable if the first permissible outer orbit of a K electron is more deeply situated for *Cu* than for other elements. To get more light on this point, the writer intends to study this problem again with the L absorption limit of the elements here considered.

In conclusion, the writer wishes to express his sincere thanks to Prof. Ishino for his kind guidance throughout the research.


Zn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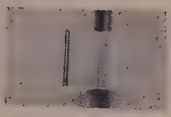
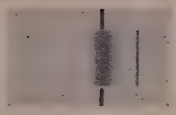
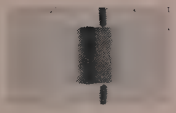

Ni


Co


Fe

Studies on the Diffusion of Metals in the Solid State, Part II

By

Shinsuke Tanaka and Chujiro Matano

(Received February 19, 1931)

Abstract

The diffusion phenomena of various metals were studied at several temperatures by observing the change in the electrical resistance of metal foils which were made by alternate electro-plating. It was concluded that the phenomena with metals which form the solid solution in all proportions not only show a similar appearance but also have nearly equal values of D, which is about 10^{-9} cm²/day at 500°C. The phenomena, however, occur in a quite different manner when the component metals do not form the solid solution.

Method of Experiment

The object of this investigation was to study the diffusion of metals in the solid state by measuring the change in the electrical resistance of strips consisting of many thin layers of two kinds of metals. The foils were made by the electro-plating of the one metal on the other, or alternately, upon wax covered with graphite, and after a suitable thickness was obtained, the foils were peeled off. Many strips of nearly 1 mm. in breadth and 15 cm. in length were cut off from them and the electrical resistance between 13.3 cm. was measured at various temperatures as in the previous experiment.[1] The electro-plating solutions had the following compositions:

100 c.c. of water containing

for silver, 1.7 gms. of silver nitrate and 0.8 gms. of potassium cyanide,

for gold, 0.17 gms. of gold chloride and 0.75 gms. of potassium cyanide,

1. S. Tanaka and C. Matano; Kyoto Coll. Sci. Mem., Vol. XIII (1930) p. 343.

for copper, 2.6 gms. of copper sulphate, 4.4 gms. of caustic soda and 13.0 gms. of Rochelle salt, and

for nickel, 5.2 gms. of nickel ammonium sulphate and 2.6 gms. of ammonium chloride, (1)

or 2.9 gms. of nickel ammonium sulphate and 1.4 gms. of boric acid. (2)

The various data of the foils are summarized in Table I.

Table I

Material	Foil	Electro-plating solution	Current density m.a./cm².	Time of each plating, min.	Number of layers	Total thickness, cm. × 10^{-3}
Ag-Au	I	Ag	3.3	10	8	2.5
		Au	1.2	30	7	
Au-Cu	II	Au	0.75	3	36	2.0
		Cu	2.15	5	37	
	III	Au	2.0	1	90	1.7
		Cu	4.0	1	90	
Cu-Ni	IV	Cu	3.7	3	50	3.4
		Ni (1)	4.5	1	50	
	V	Cu	3.7	1/2	150	3.0
		Ni (1)	5.5	1/3	150	
Ag-Ni	VI	Ag	3.5	20	6	4.6
		Ni (1)	4.5	20	6	
	VII	Ag	3.7	1	75	5.1
		Ni (1)	4.5	1	75	
	VIII	Ag	3.7	1	75	3.0
		Ni (2)	4.5	1	75	
Ag-Cu	IX	Ag	3.8	1/2	100	4.2
		Cu	3.8	5/6	100	

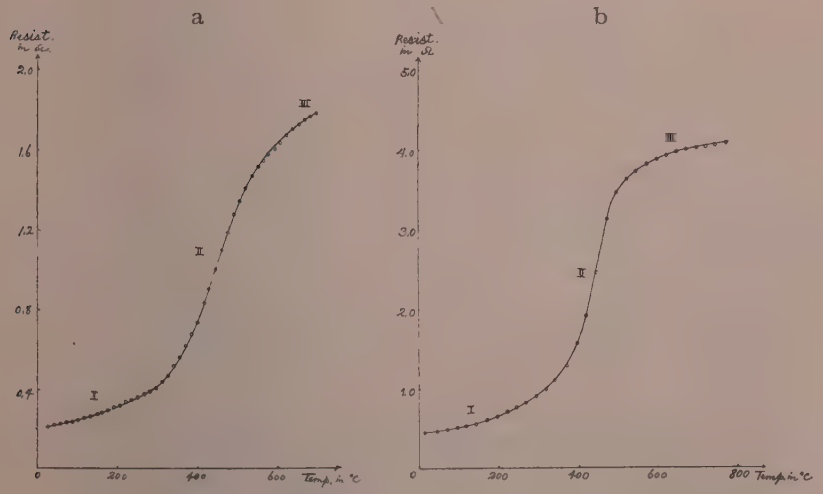
Results of Experiments

The first experiment: The samples were examined by taking X-ray photographs of them before and after heating, and the formation of the alloy confirmed. The Debye-Scherrer camera of a Müller spectrograph was used and the X-rays were obtained from a Shearer metal tube with copper anticathode excited by a transformer; about 40—50 K.V. and 3—4 m.a. output. The exposure was about 5 hours. The photographs obtained from Foil IV are reproduced in Fig. I, Plate I, for illustration, Ia being the one taken before heating, and Ib that after heating. (In the case of Foil I the examination was not carried out, since the lattice constants of gold and silver are nearly the same.) The distributions of the spectral lines clearly show the formation of an alloy on heating the sample.

In the case of Foil IX scarcely any difference was observed between the photographs taken before and after heating.

The second experiment: The electrical resistances of all the samples were measured by raising the temperature at a suitable rate in order to study the relation between the diffusion and temperature. The

Fig. 2

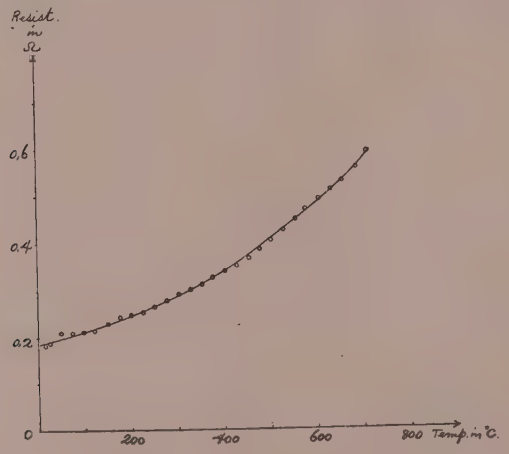


curves in Fig. 2 showed the results given by the samples (mass of 32.5 mgms. or 15.7 mgms.) which were obtained from Foils I and IV. In the former case the temperature was raised 3 degrees per

minute and in the latter 5 degrees per minute. There are three stages I, II and III as in the case of the Au-Cu system of the previous experiments[1] and they can be explained in the same way, i. e. the first stage indicated the temperature effect on the pure metals, the second stage the effect of temperature and diffusion, and the third stage the effect of temperature on the alloy. These systems always form the solid solution and all the samples showed the same nature.

Next a quite different form in the change of the electrical resistance was observed when the samples obtained from Foils VII, VIII and IX were examined. In these cases there could not be found any rapid change in the resistance. The result of the sample (mass of 30.0 mgms.) obtained from Foil IX is, for instance, represented by the curve shown in Fig. 3, from which the general features will be recognized. These systems do not form the solid solution with all portions of the component metals, and this seems to be the cause of the above difference.

Fig. 3

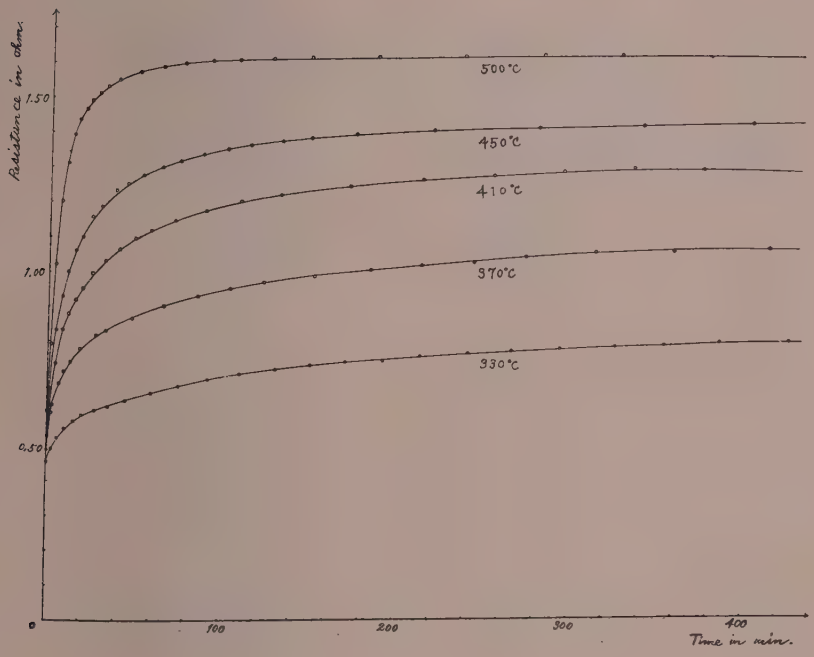


The third experiment: The change in the electrical resistance at various constant temperatures was observed in order to study how the diffusion is related to time. The results for samples (mass of 30.0 mgms.) obtained from Foil I and samples (mass of 15.0 mgms.) from Foil IV are shown by the curves in Fig. 4a and Fig. 4b respectively.

1. S. Tanaka and C. Matano. loc. cit.

There will also be found a similarity with the case of the Au-Cu system in the previous experiment.

Fig. 4 a



When, however, samples obtained from Foils VI, VII and IX are taken, the results seem to be somewhat different from the above ones. In the case of the Ag-Ni system no change in the electrical resistance due to diffusion could be observed, as is shown in Fig. V, which was given by the samples (mass of 30.0 mgms.) from the Foil VI. This difference must be due to the mechanism of making the alloy or to diffusion, and further investigation will be needed for these points.

Determination of Diffusion-Coefficient

The coefficient of diffusion for the Ag-Au system given by Fick's law has already been determined at 500°C by these authors.[2] A similar

2. Phys. Math. Soc. Japan. Proc., Vol. 12, (1930) p. 279.

Fig. 4 b

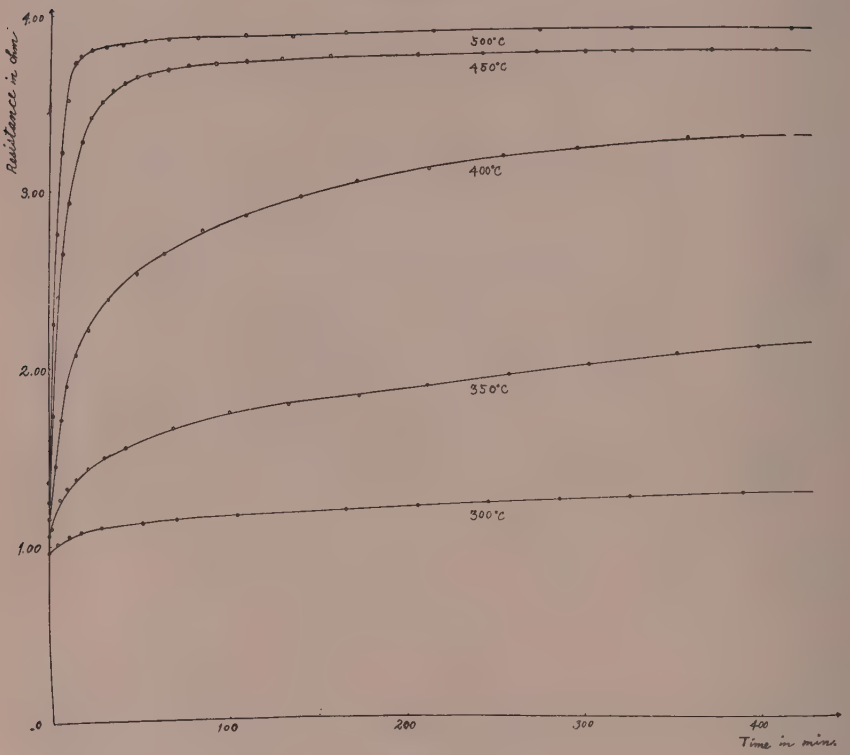
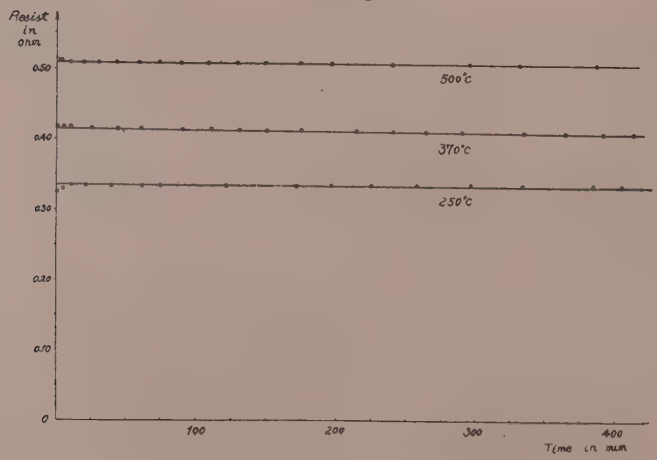

Resistance in ohm
4.00
3.00
2.00
1.00
.0
500°C
450°C
400°C
350°C
300°C
100
200
300
400
Time in mins

Fig. 5

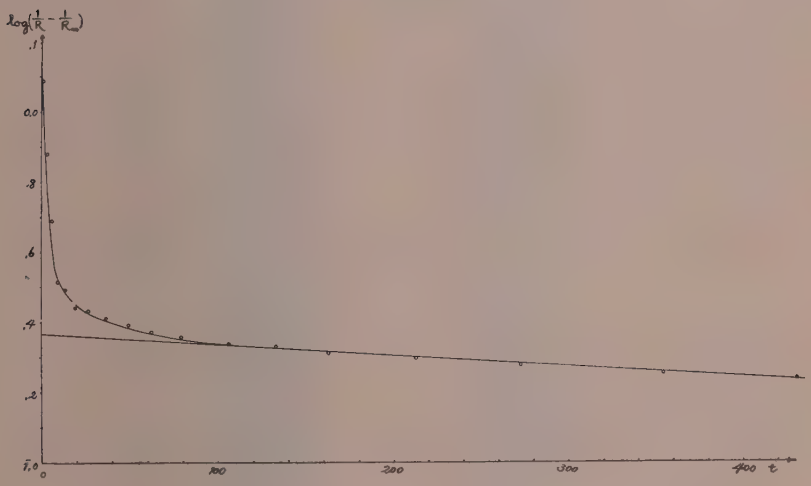

Resist in ohm
0.50
0.40
0.30
0.20
0.10
0
500°C
370°C
250°C
100
200
300
400
Time in min

consideration was utilised to determine those of the Au-Cu and Cu-Ni systems. In the third experiment, in the above section, let the resistance at time t be R and that at $t \to \infty$ (in practice, it is sufficient if we take t sufficiently great) R_∞, then there exists the following relation in the proper range of time,

$$\log(1/R - 1/R_\infty) = \text{const.} - 2D(\pi/d)^2 \log e \cdot t,^1$$

where D is the coefficient of diffusion, d the mean thickness of each layer, π the modulus of circumference, e the base of natural logarithms, and consequently $2\pi^2 \log e = 8.56$. The above equation shows a straight line and D can be determined from its slope.

Fig. 6



The authors show, as an example, the curve for the sample (mass of 16.5 mgms.) from Foil IV in Fig. 6, from which D can be obtained at once.

The values of D for other samples were determined at 500°C in this way and are tabulated in Table II.

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1. The factor 2 in this expression must be multiplied because the value of E_1 is generally equal to zero and E_2 is not zero in the expression $K = \Sigma E_n e^{-n\beta t}$ of the previous paper cited in (2).

Table II

Material	Foil	Thickness of each layer d, cm.	Coefficient of diffusion D, $cm^2./min.$	D mean $cm^2./min.$
Au-Cu	II	2.8×10^{-5}	1.0×10^{-12}	0.6×10^{-12}
	III	9.5×10^{-6}	0.3×10^{-12}	
Cu-Ni	IV	3.4×10^{-5}	0.4×10^{-12}	0.7×10^{-12}
	V	1.0×10^{-6}	1.0×10^{-12}	

Since the value of D for the Au-Ag system which was obtained in the previous experiment is about $0.8\times10^{-12}cm^2./min.$, the conclusion seems to be that all the coefficients of diffusion have nearly equal values for metals which make the solid solution in all proportions.

In conclusion the authers wish to express their sincere thanks to Prof. U. Yoshida for his cordial advice and to Mr. S. Hirose for his kind assistance in this work.

Physical Laboratory,
The Osaka University of Engineering,
December 25, 1930.

Fig. 1 a

Fig. 1 b

X-ray Diffraction of Some Organic Substances in the Solid and liquid States

By

Shinsuke Tanaka, Genjiro Okuno and Akira Tsuji

(Received February 20, 1931)

Abstract

Of five organic substances, powder patterns were compared with liquid patterns. The results are as follows; (1) Corresponding to the intense lines in the crystal patterns, there appear liquid bands, (2) If these crystal lines keep at moderate distances from one another, we get separate liquid bands corresponding to each of them, (3) If these crystal lines lie close together, corresponding to them we get a broad and diffuse band in the liquid state. From these characters it may be concluded that the crystal planes which produce the intense reflection seem to maintain their properties when the crystal becomes liquid.

Investigations of the relations between the crystal and liquid patterns have already been performed with many substances. Eastman[1] investigated them with benzene, Herzog and Jancke[2] with more than twenty organic substances. P. Krishnamurti[3] also investigated them with some di-substituted benzene derivatives and some other aromatic hydrocarbons and he pointed out some relations between the crystal dimensions and data derived from the liquid patterns.

The object of the present investigation is to study how the crystal lines are related to the liquid bands, by which means the structure of a liquid seems likely to be cleared up in some degree. The deeper investigation of the subject has, however, been left for the future.

1. Eastman, J. Amer. Chem. Soc., **46**, 917, 1924.
2. Herzog and Jancke, ZS. f. Phys., **45**, 194, 1927.
3. P. Krishnamurti, Ind. J. Phys., **3**, 225. 1928; also **5**, 543. 1930.

Experiment and Results

The experimental apparatus and working conditions were almost the same as in the previous experiment.[1] The Shearer metal tube with copper anticathode was now evacuated with the mercury diffusion-pump and excited at about 55 kilovolts, the current through the tube being 3.2—4.2 milliamperes. The time of exposure was 4—6 hours for solids, and 6—9 hours for liquids. The sample was sealed in a thin glass tube 1 mm. in diameter. Many photographs corresponding to various temperatures were taken with samples in the solid state, all of which showed that the crystal lines did not change their appearance until the melting point was reached. The liquid patterns were photographed at the temperature of 10—20°C above the melting point. The substances now studied were Phenanthrene[K], α-Naphthol[M], β-Naphthol[K], α-Naphthylamine[M] and β-Naphthylamine[K][2]. The spacings corresonding to the important crystal lines and liquid bands were calculated from Bragg's formula and are shown in the tables given below.

Phenanthrene[3]: In the powder photographs, there can be seen one intense line near the direct incident ray, and apart from this, three intense lines lying close together and keeping almost equal distances. There are two liquid bands; both are very broad and diffuse and are observed with difficulty. The inner band, with the maximum intensity at the spacing 8.55 A.U., corresponds to the crystal line near the direct incident ray, and the outer band, with the maximum intensity at the spacing 4.50 A.U., covers the range from 5.07 A.U. to 3.45 A.U. in the powder pattern. The other fainter lines in the powder pattern are lost in the general scattering in the case of the liquid one.

α- and β-Naphthol: For the α-Naphthol there appear two fairly sharp liquid bands, corresponding to the two intense crystal lines. Besides, at a small angle, there seems to exist a third faint band.

β-Naphthol has an intense line in the crystal pattern and shows only one liquid band, the sharpness of which is nearly equal to that of the band of α-Naphthol. There is, also, a moderate amount of scattering at small angles in the liquid pattern.

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1. Tanaka and Tsuji, These Memoirs, **13**, 337. 1930.
2. The letters attached to the names of the samples mean "Merck" and "Kahlbaum", the manufacturers.
3. P. Krishnamurti, loc. cit. (the latter)

In the tables we use the following abbreviations:
v.s.=very strong, s.=strong, m.s.=medium strong,
w.=weak, v.w.=very weak.

Table 1. Phenanthrene

Powder		Liquid		
Spacing(A.U.)	Intensity	Angle of Diffraction	Spacing(A.U.)	Intensity
9.63	m.s.	10°22′	8.55	s.
5.59	v.w.	16°51′	5.23	Inner limit of outer band.
5.07	v.s.			
4.50	v.w.	19°39′	4.50	m.s.
4.10	s			
3.45	s	27°20′	3.26	Limit of general Scattering.
2.57	v.w.			

Table 2. α- and β-Naphthol

State / Sample	Powder		Liquid		
	Spacing(A.U.)	Intensity	Angle of Diffraction	Spacing(A.U.)	Intensity
α-Naphthol	5.80	s.	14°21′	6.18	s.
	4.59	v.w.			
	4.01	w.	22°29′	4.03	m.s.
	3.80	s.			
	3.24	w.			
	2.97	v.w.			
	2.74	v.w.			
β-Naphthol	8.11	w.			
	5.10	w.	17° 6′	5.18	s.
	4.53	v.s.			
	4.15	m.s.			
	3.72	w.	23°16′	3.85	Limit of general Scattering.
	3.35	w.			
	2.68	v.w.			

α- and β-Naphthylamine: α-Naphthylamine has again two liquid bands of fair sharpness which correspond to two intense crystal lines. Besides, the liquid pattern seems to have a third faint band at the position corresponding to that of the crystal line 10.41 A.U. in spacing, though this cannot be definitely stated.

β-Naphthylamine has characters analogous to those of β-Naphthol. It has only one liquid band, which is more diffuse at the outer side than at the inner.

Table 3. α- and β-Naphthylamine

State / Sample	Powder		Liquid		
	Spacing(A.U.)	Intensity	Angle of Diffraction	Spacing(A.U.)	Intensity
α-Naphthylamine	10.41	m.s.			
	6.13	w.	14°53′	5.93	m.s.
	4.90	s.			
	4.12	w.	22°40′	3.93	w.
	3.67	s.			
	3.13	v.w.			
β-Naphthylamine			17° 7′	5.17	m.s.
	4.76	s.			
	4.24	w.			
	3.78	w.	24°28′	3.64	Limit of general Scattering
	3.44	m.s.			
	2.90	w.			
	2.48	v.w.			

Summary

From the data above mentioned we can deduce the following conclusions:

1. A substance which shows only one intense crystal line gives one fairly sharp band in the liquid pattern. (β-Naphthol).

2. One which gives two intense crystal lines moderately separated, gives two corresponding liquid bands of fair sharpness. (α-Naphthol).

3. When two or more intense crystal lines lie close together, we get a broad band in the liquid state which has its maximum intensity at the position corresponding to that of the most intense crystal line, and which is more diffuse at the side where the less intense lines are situated. (β-Naphthylamine, Phenanthrene).

4. Even when two intense crystal lines lie pretty close together, we have two separate liquid bands, if they are of the same intensity. (α-Naphthylamine).

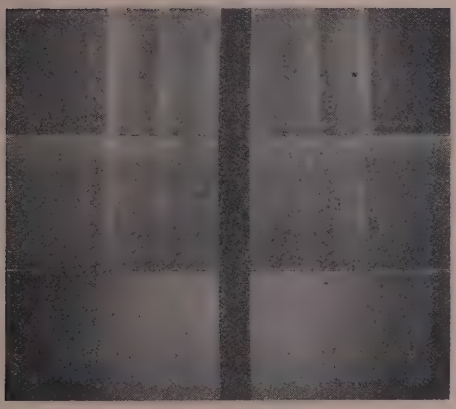
5. The spacing corresponding to the position of the maximum intensity in the liquid band is generally greater than that of the corresponding crystal line except in the case of phenanthrene.

6. It may be concluded that the crystal planes which produce the intence reflection seem to maintain their properties when the crystal becomes liquid.

In conclusion the writers wish to express their hearty thanks to Prof. M. Ishino for the interest he has taken in the research.

Physical Laboratory,
The Osaka University of Engineering,
January 16, 1931.

α-Naphthol

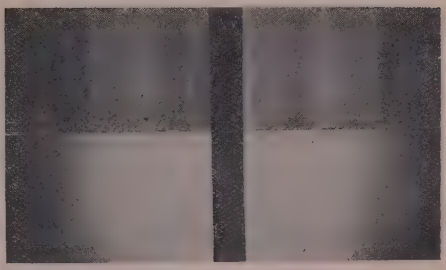


28°

90°

25°

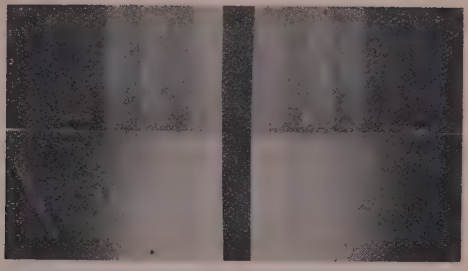
Phenanthrene



90°

110°

α-Naphthylamine



20°

70°

β-Naphthol

22°

05°

40°

β-Naphthylamine

16°

100°

120°

A New Method for Determining Tin and Antimony in their Mixture

By

Gisho Sakurada

(Received February 28, 1931)

Since tin and antimony may, without much difficulty, be transformed into the oxide forms it occurred to the writer that this property might in some way be utilized for the quantitative determination of these metals existing as a mixture. Following up this idea, he transformed the two metals simultaneously into a mixture of their oxides by treating them with concentrated nitric acid, and the oxide mixture thus formed was ignited at 800°–820° C. for half an hour, and weighed. The mixture, which was presumed to contain tin in the form of SnO_2 and antimony in that of Sb_2O_4 was now treated with potassium iodide in a tartaric-hydrochloric acid solution in order to reduce antimony to the antimonous state and the antimony thus reduced was determined iodometrically. As is shown in the experimental part, the results turned out fairly satisfactory, showing that the method above described is applicable to practical purposes. The experiments were further extended to the case in which tin and antimony form a mixture with another metal such as copper, and in this case too a tolerably good result was obtained.

Experimental Part

I. Analysis of a sample consisting only of tin and antimony

In the experiment tin and antimony obtained from Kahlbaum were used. The purity of the former was confirmed to be 99.95% and that of the latter 99.98%. About 0.2—0.25 grams of various mixtures containing the two metals in different proportions were weighed out, and left to stand with 10 c.c. of conc. HNO_3 and a few c.c. of water

till the fumes of nitric oxide ceased to be evolved, whereupon the excess of nitric acid was evaporated off and the residue was made slightly alkaline with ammonia and again evaporated to dryness. The mixture of oxides was then transferred to a crucible and heated gradually to 800°—820° C. at which it was maintained for about half an hour. The heating was repeated till the weight became constant. To the oxide mixture were next added 5—10 c.c. of 10% potassium iodide solution, 3—5 grams of tartaric acid, 40 c.c. of 12N-HCl, 0.3 grams of potassium chloride and 10 c.c. of water, and the mixture was heated in a sand-bath. By this treatment the antimony in the Sb_2O_4 was reduced and dissolved as antimonous chloride, iodine being liberated at the same time, thus,.....

$$Sb_2O_4 + 6HCl + 2HI = 2SbCl_3 + 4H_2O + I_2.$$

The heating having been continued till all the iodine was nearly evaporated off, the solution was treated with a few drops of dil. sodium thiosulphate solution in order to get rid off the last trace of iodine, and neutralized with a caustic soda or sodium carbonate solution. The solution was then diluted to 200 c.c. and a saturated solution of sodium bicarbonate, which must be taken in the proportion of 10 c.c. to every 0.1 gram of metallic antimony, was added to it. With the solution thus prepared, antimony was titrated iodometrically with 1/10N-iodine solution. From the weight of the antimony, the weight of the Sb_2O_4 was calculated by multiplying it by the factor 1.2663, and the amount of the SnO_2 and therefore that of the tin present in the mixture were calculated by subtracting the weight of the Sb_2O_4 from the total weight of the mixed oxide. The results are shown in Table I.

Table I

No.	Sn gms.	Sb gms.	Sn %	$SnO_2+Sb_2O_4$ gms.		Diff. gms.	Sb gms. Found	Diff. gms.
				Calc.	Found			
1	0.0236	0.2123	10	0.2988	0.2986	−0.0002	0.2120	−0.0003
2	0.0400	0.1597	20	0.2530	0.2531	+0.0001	0.1600	+0.0003
3	0.0672	0.1575	30	0.2848	0.2850	+0.0002	0.1573	−0.0002
4	0.0875	0.1305	40	0.2764	0.2766	+0.0002	0.1304	−0.0001
5	0.1046	0.1043	50	0.2648	0.2654	+0.0006	0.1040	−0.0003
6	0.1163	0.0782	60	0.2467	0.2482	+0.0015	0.0779	−0.0004
7	0.1367	0.0589	70	0.2481	0.2498	+0.0017	0.0589	±0.0000?
8	0.1743	0.0445	80	0.2776	0.2784	+0.0008	0.0450	+0.0005?

As is seen in the above table, the value of the two oxides is always too high when the content of tin in the mixture becomes greater than 60%. Probably this is due to the fact that the conversion of tin oxide into the form of SnO_2 is not complete at 800°—820°C. The error thus produced is, however, insignificant, when the content of tin is less than 50%.

Several experiments were conducted to learn how the dehydration of tin oxide is governed by the temperature, and the results shown in Table II were obtained.

Table II

0.2037 gram of tin corresponding to 0.2586 gram of SnO_2 were employed.

Temperature	Time of ignition in minutes	SnO_2 Found	Diff.
780°	20	0.2639	+0.0053
820°	15	0.2600	+0.0014
„	30	0.2600	„
850°	20	0.2587	+0.0001
870°	20	0.2587	„

There are several reports on the temperature suitable for the conversion of Sb_2O_5 into Sb_2O_4. According to H. Bilz,[1] Sb_2O_5 changes into Sb_2O_4 at 450° and the latter into Sb_2O_3 at 1060°. T. Carnelly and T. Walker[2] state that Sb_2O_4 is stable between 585°—775°, while Baubigny[3] regards the temperature between 750°—850° as the best for the quantitative conversion of Sb_2O_5 into Sb_2O_4, which gradually changes into volatile Sb_2O_3 at temperatures higher than 950°. The results of the present author's experiments were found to agree with those of Baubigny comparatively well. The transformation of Sb_2O_5 into Sb_2O_4 was found to proceed very slowly at 750° and only at 800°—820° to become very significant. When, however, the temperature was raised higher than 840°C, loss due to the formation of Sb_2O_3 was unavoidable as is seen in Table III.

1. H. Bilz: Z. f. phys. Chem., **19**, 385, 1896.
2. T. Carnelly & T. Walker: J. Chem. Soc., **53**, 86, 1888.
3. Baubigny: Compt. rend., **124**, 499, 1897.

Table III

Sb_2O_4 gms.	Temperature	Time of ignition in minutes	Loss in weight gms.
0.3178	840°	30	0.0036
0.0250	850°	10	0.0095
0.2429	850°	30	0.1534

Though stannic tin is not reduced by hydrogen iodide, the end point in the titration of antimony becomes indistinct unless some tartaric acid is added to the solution. In the solution in which tin exists in a large excess, titration of antimony cannot be conducted accurately even in the presence of tartaric acid, as is shown in Table IV.

Table IV

Sb used : 0.1090 gm.

Sn gms.	Tartaric acid gms.	Sb gms. Found	Diff.	Remarks
0.05	3	0.1090	±0.0000	
0.1	0	0.1044—0.1055	—0.0046—35	End point somewhat indistinct.
„	3	0.1088	—0.0002	
0.2	5	0.1089	—0.0001	
0.3	5	0.1087	—0.0003	
0.4	0	—	—	End point indistinct.
„	5	0.1073?	—0.0017?	Somewhat indistinct.
„	7	0.1084?	—0.0006?	„

II. Analysis of a sample containing some other metals besides tin and antimony.

To see how the above method for determining tin and antimony can be applied to the analysis of a sample containing other metals also, an alloy consisting of tin, antimony and copper was analysed in the following way :—

0.3 gram of the alloy was dissolved in 40 c.c. of concentrated

hydrochloric acid containing some bromine, and the solution, after having been concentrated to 20 c.c. in a water-bath, was neutralized with caustic soda and diluted to 150 c.c. Now 50—100 c.c. of the sodium sulphide solution prepared by dissolving 60 gms. of $Na_2S\ 9H_2O$ and 40 gms. of NaOH in 1000 c.c., 3—5 gms. of tartaric acid and 5 c.c. of a saturated solution of sodium acetate were added to the solution and the whole heated in a sand bath till copper sulphide had completely subsided. It was then filtered and the precipitate was washed with water containing sodium acetate and sodium sulphide, and the filtrate together with the washings was acidified with HCl so as to precipitate the sulphides of tin and antimony. To make the precipitation of the sulphides complete, 10 c.c. of a saturated solution of ammonium nitrate was added to the solution in which the sulphides were suspended and a current of hydrogen sulphide was passed into it. The sulphides were then filtered and washed as usual and dried. The dried precipitate[1] was left to stand in a closed vessel containing some fuming nitric acid, in order to expose the precipitate to a nitric acid gas atmosphere. By this treatment the sulphides were gradually oxidized, sulphur being set free. After the nitric acid still adhering to the precipitate had been driven off, the precipitate was washed with alcohol and carbon bisulphide and then with alcohol and ether successively, and finally ignited in a crucible. It is here to be noted that the ignition must be conducted at first very gradually, otherwise the sulphur still remaining acts upon the oxides in the manner represented in the following equations, before it is completely oxidized to sulphur dioxide :—

$$SnO_2 + 3S = SnS_2 + SO_2$$
$$Sb_2O_4 + 5S = Sb_2S_3 + 2SO_2.$$

When the evolution of sulphur dioxide had ceased the temperature was raised to 800°—820° and the heating was continued till the weight became constant. Sometimes sulphuric acid formed by oxidation obstinately adheres to SnO_2. In such a case a small quantity of ammonium carbonate should be added and ignited. The results were as shown in Table V.

---

1. Sulphides adhering to the filter-paper were removed by dissolving them in ammonium sulphide and recovered by evaporating the ammonium sulphide solution to dryness.

Table V

No.	Sn gms.	Sb gms.	Sn %	$SnO_2+Sb_2O_4$ gms.		Diff. gms.	Sb gms. Found	Diff. gms.
				Calc.	Found			
1	0.0188	0.1692	10	0.2381	0.2378	−0.0003	0.1690	−0.0002
2	0.0475	0.1901	20	0.3010	0.3006	−0.0004	0.1899	−0.0002
3	0.1184	0.1185	50	0.3004	0.3002	−0 0002	0.1179	−0.0006
4	0.1820	0.0454	80	0.2886	0.2917	+0.0031	0.0454?	±0.0000?

The author takes this opportunity warmly to thank Professor Motooki Matsui, under whose guidance and encouragement this work was carried out.

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CONTENTS

Quantitative Spectrum Analysis
By Arata Iwamura 43

Relation between the *K* Absorption Edge and the K_{β_2} Line of *Ni*, *Cu* and *Zn*
By Suekichi Kawata 55

Studies on the Diffusion of Metals in the Solid State, Part II
By Shinsuke Tanaka and Chujiro Matano 59

X-ray Diffraction of Some Organic Substances in the Solid and liquid States
By Shinsuke Tanaka, Genjiro Okuno and Akira Tsuji . . 67

A New Method of Determining Tin and Antimony in their Mixture
By Gisho Sakurada 73